

# PATENT SPECIFICATION

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(19)



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## (54) NICKEL BASE ALLOY CONTAINING HAFNIUM

(71) We, AVCO CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America, of Suite 1800, 1014 Vine Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to nickel base alloys exhibiting high strength, stability, ductility and resistance to corrosion, sulfidation and oxidation at elevated temperatures and which are useful for blades, vanes and integrally cast turbine wheels.

The nickel base alloys of this invention contain relatively small, but nonetheless significant, amounts of tungsten and molybdenum for solid solution strengthening; chromium for oxidation and sulfidation resistance; tantalum for solid solution and carbide strengthening; aluminum and titanium to enhance the strength by precipitation of a fine dispersed phase, gamma prime (Ni<sub>3</sub>(Al, Ti)), and hafnium for intermediate strength, ductility and improved oxidation resistance.

Compositions of the following analyses are contemplated as within the scope of the present invention the compositions being expressed in weight percent, the balance being Ni except for incidental impurities:

C	—	0.30 max.	Hf	—	0.1—3
Cr	—	11—15	Ti	—	3.5—4.5
Co	—	8—12	Al	—	3—4
Mo	—	1—2.5	Ti + Al	—	7—8
W	—	3—10	B	—	0.005—0.025
Ta	—	3.5—10	Zr	—	0.05—0.4

balance Ni

A more preferred range of composition is as follows:

C	—	.25 max.	Hf	—	0.4—3
Cr	—	11—13.5	Ti	—	3.5—4.5
Co	—	8—11	Al	—	3—4
Mo	—	1—2.5	Ti + Al	—	7—8
W	—	3—5	B	—	0.005—0.025
Ta	—	3.5—8	Zr	—	0.05—0.4
			Balance Ni		

A still more preferred range of compositions is as follows (in weight percent):

5	C	—	0.10—0.22	Hf	—	0.75—1.25
	Cr	—	12.2—13.5	Ti	—	3.9—4.2
	Co	—	8.5—9.5	Al	—	3.2—3.6
	Mo	—	1.85—2.05	Ti + Al	—	7.25—7.70
	W	—	3.65—8	B	—	0.01—0.02
10	(preferably 3.65—4.05)			Zr	—	.08—.25
	Ta	—	3.65—8			
	(preferably 3.65—4.05)					
	balance Ni					

Exemplary alloys in accordance with the teachings of this invention had the compositions shown in Table I which follows:

TABLE I

Heat No.	C	Cr	Ce	Mo	W	Ta	Hf	Ti	Al	Ti+Al	B	Zr	Ni
I	.15	12.50	9.35	1.94	3.99	3.86	1.10	3.96	3.57	7.53	.015	.17	Bal
II	.15	12.50	9.35	1.94	3.99	3.86	2.28	3.96	3.57	7.53	.015	.21	Bal
III	.23	12.80	8.68	1.97	4.00	3.77	0.49	4.32	3.28	7.60	.016	.13	Bal
IV	.23	12.38	8.68	1.97	4.00	3.77	1.07	4.32	3.28	7.60	.016	.16	Bal
V	.23	12.38	8.68	1.97	4.00	3.77	1.55	4.32	3.28	7.60	.016	.14	Bal
VI	.23	12.38	8.68	1.97	4.00	3.77	1.80	4.32	3.28	7.60	.016	.20	Bal
VII	.23	12.38	8.68	1.97	4.00	3.77	0.44	4.32	3.28	7.60	.016	.14	Bal
VIII	.20	12.31	9.18	1.94	3.72	4.05	1.06	4.08	3.38	7.46	.014	.15	Bal
IX	.20	12.31	9.18	1.94	3.72	4.05	2.26	4.08	3.38	7.46	.014	.22	Bal
X	.20	12.31	9.18	1.94	3.72	4.05	2.16	4.08	3.38	7.46	.014	.21	Bal
XI	.20	12.31	9.18	1.94	3.72	4.05	1.16	4.08	3.38	7.46	.014	.16	Bal
XII	.19	12.66	9.42	1.92	3.75	3.86	2.40	4.01	3.27	7.28	.015	.22	Bal
XIII	.15	12.50	8.88	2.04	3.95	5.0	1.13	3.96	3.22	7.18	.013	.10	Bal
XIV	.15	12.50	8.88	2.04	3.95	6.0	1.13	3.96	3.22	7.18	.013	.10	Bal
XV	.20	13.35	8.88	1.91	3.87	8.0	1.20	4.18	3.21	7.39	.012	.11	Bal

TABLE I (cont'd)

Heat No.	C	Cr	Co	Mo	W	Ta	Hf	Ti	Al	Ti+Al	B	Zr	Ni
XVI	.20	13.35	10.88	1.91	3.87	6.0	1.20	4.18	3.21	7.39	.012	.11	Bal
XVII	.20	13.35	10.88	1.91	3.87	7.0	1.20	4.18	3.21	7.39	.012	.11	Bal
XVIII	.20	13.35	10.88	1.91	3.87	8.0	1.20	4.18	3.21	7.39	.012	.11	Bal
XIX	.15	12.87	9.49	2.01	4.01	4.0	1.05	4.10	3.23	7.33	.013	.11	Bal
XX	.15	12.87	9.49	2.01	5.01	7.50	1.05	4.10	3.23	7.33	.013	.11	Bal
XXI	.15	12.87	9.49	2.01	7.50	5.0	1.05	4.10	3.23	7.33	.013	.11	Bal
XXII	.15	12.87	9.49	2.01	10.0	5.0	1.05	4.10	3.23	7.33	.013	.11	Bal
XXIII	.16	12.60	9.40	2.0	3.97	3.85	0.50	4.0	3.55	7.55	.020	.10	Bal
XXIV	.21	12.80	9.40	2.19	4.0	4.08	1.95	4.05	3.25	7.30	.014	.10	Bal
XXV	.21	12.80	9.40	2.19	4.0	4.08	1.95	4.05	3.25	7.30	.014	.15	Bal
XXVI	.21	12.80	9.40	2.19	4.0	4.08	1.95	4.05	3.25	7.30	.014	.20	Bal
XXVII	.09	12.30	9.10	1.87	7.40	4.94	1.25	4.18	3.35	7.53	.012	.12	Bal
XXVIII	.09	12.30	9.10	1.87	4.90	4.94	1.25	4.18	3.35	7.53	.012	.12	Bal
XXIX	.27	12.40	9.00	1.87	7.40	4.90	1.15	4.06	3.20	7.26	.013	.11	Bal

5 After vacuum melting, the alloys noted  
above were vacuum cast into test bars and sub-  
jected to stress rupture testing according to  
ASTM Standard E139. The test bars were  
10 heat treated before testing as follows: heated to  
2050°F, held at that temperature for two (2)  
hours then air cooled, then reheated to 1550°F  
and held at 1550°F for four (4) hours, then  
air cooled, then reheated to 1400°F and held  
10 at that temperature for 16 hours then air  
cooled.

15 After the heat treatment described above,  
stress rupture tests were conducted on cast  
test bars representative of each of the heats  
in the heat treated condition at 1400°F/

90Ksi, 1400°F/100Ksi, 1700°F/39Ksi and  
1800°F/29Ksi. The results are given in Table  
II, it being noted that thickwall data refers to  
0.250" diameter solid test bar results. Thin-  
wall data refers to tubular test bar results in  
20 which wall thickness is 0.040". Thickwall or  
solid test for data reflects mechanised property  
capability of heavy sections such as might be  
represented by turbine blade roots. Thin wall  
25 or tubular test bar properties reflect the  
mechanical property capabilities of thin walled  
sections such as might be represented by cored  
or hollow turbine blade airfoils. Thinwall data  
are for tests at 1700°F/35Ksi.

TABLE II  
STRESS RUPTURE TEST RESULTS

Heat No.	1400°F/90Ksi Life (Hrs.)	1400°F/90Ksi El (%)	1400°F/95Ksi Life (Hrs.)	1400°F/95Ksi El (%)	THICKWALL 1400°F/100Ksi Life (Hrs.)	THICKWALL 1400°F/100Ksi El (%)	1700°F/39Ksi Life (Hrs.)	1700°F/39Ksi El (%)	1800°F/29Ksi Life (Hrs.)	1800°F/29Ksi El (%)	THINWALL 1700°F/35Ksi Life (Hrs.)	THINWALL 1700°F/35Ksi El (%)
I	462	4	163	3			72	5				
	483	5					99	5				
II			382	7			79	9				
III			225	5			99	10				
			87	10			106	10				
IV			211	5			106	10				
			180	5								
V			73	3								
			119	5			48	8				
VI			208	4			77	9				
VII	277	4					65	7				
	419	5					121	3				
VIII	286	5.5					50	8				
	408	6					37	6				
IX	530	3					45	10				
							38	6				
							36	7				

TABLE II (cont'd)  
STRESS RUPTURE TEST RESULTS

Heat No.	1400°F/90Ksi Life (Hrs.)	1400°F/90Ksi El (%)	1400°F/95Ksi Life (Hrs.)	1400°F/95Ksi El (%)	THICKWALL 1400°F/100Ksi Life (Hrs.)	1400°F/100Ksi El (%)	1700°F/39Ksi Life (Hrs.)	1700°F/39Ksi El (%)	1800°F/29Ksi Life (Hrs.)	1800°F/29Ksi El (%)	THINWALL 1700°F/35Ksi Life (Hrs.)	1700°F/35Ksi El (%)
X	505.7	7.5					71	8				
							50	6				
XI	273	4					56	7				
							60	7.5				
XII			160	8			97	8.0				
			153	6								
XIII					97	5	88	6	44	5		
									61	6		
XIV					159	5	129	9	61	8		
									58	5		
XV					70	4	53	4	48	6		
					45	3	56	4	49	6		
					49	3						
XVI					104	8	62	7	22	8		
							63	8	27	10		

TABLE II (cont'd)  
STRESS RUPTURE TEST RESULTS

Heat No.	1400°F/90Ksi		1400°F/95Ksi		THICKWALL 1400°F/100Ksi		1700°F/39Ksi		1800°F/29Ksi		THINWALL 1700°F/35Ksi	
	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)
XVII					130	8	93	7	38	10		
									45	9		
XVIII									35	9		
									37	8		
XIX					130	9	72	9			53	6
					103	8					58	6
XX					149	4			50	6	64.4	6.0
					174	4			28	9	70.6	5.0
											178.0	5.0
XXI					142	4			43	10	129	5
					224	5			79	5	189	5
									81	7	254	5
XXII					224	5			45	5	101	N/A
									51	8	137	6
XXIII	113	4					39	4				
	116	3					67	4				

N.A Not Available.



TABLE II (cont'd)  
STRESS RUPTURE TEST RESULTS

Heat No.	1400°F/90Ksi		1400°F/95Ksi		THICKWALL 1400°F/100Ksi		1700°F/39Ksi		1800°F/29Ksi		THINWALL 1700°F/35Ksi	
	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)
XXIV					144	9	109	10				
					167	6	88	10				
							99	10				
XXV					181	15	65	N/A				
							71	8				
XXVI					172	6	79	10				
					168	8	83	8				
							80	9				
XXVII					163	5			59	8	60	3
					157	7			58	5	68	4
XXVIII					130	4	119	8	60	10	111	5
					212	6	75	9	61	9	125	5
											125	9
XXIX					110	4			81	5	122	4
					133	5			61	8	184	4
											212	5

N.A. Not available.

TABLE II (cont'd)  
STRESS RUPTURE TEST RESULTS

Heat No.	1400°F/90Ksi		1400°F/95Ksi		THICKWALL 1400°F/100Ksi		1700°F/29Ksi		1800°F/29Ksi		THINWALL 1700°F/35Ksi	
	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)	Life (Hrs.)	El (%)
INCO 713	16	6	5	4			20	12				
MAR-M- 421	50	3	20	3			15	15				
IN792	255	7.5			75	7	75	3				

Corresponding values for three presently known commercial alloys are appended to Table II for comparison.

5 INCO 713C is reported to be an alloy with a nominal composition of

C Cr Mo W Cb Ti Al  
0.14 13.0 4.5 0.20 2.0 0.75 5.75

Zr B Ni  
0.05 0.012 Balance

10

MAR-M-421 is reported to be an alloy with

a nominal composition of

C Cr Co Mo W Cb Ti Al  
0.15 15.8 9.5 2.0 3.8 2.0 1.8 4.3

Zr B Ni  
0.05 0.015 Balance

INCO IN792 is reported to be the alloy described in United States Patent 3,619,182.

Table III presents the room temperature tensile properties of the alloy of this invention, heat treated as before, after casting into test bars.

20

TABLE III  
ROOM TEMPERATURE TENSILE TEST RESULTS

Heat No.	Uts. (Ksi)	0.2% Y <sub>2</sub> S. (Ksi)	(%)	R.A. (%)
VIII	181.4	169.2	3.5	3.2
	172.5	163.9	3.5	3.2
INCO-713C	123	106	7.9	11.6
MAR-M-421	150	130	3.5	5

Comparable values for the same commercial alloys are appended to the table for comparison.

- 5 In the Tables IV and V respectively, data is presented on cyclic oxidation test results conducted at 1750°F and hot corrosion test conducted at 1650°F.

10 TABLE IV  
COMPARATIVE CYCLIC OXIDATION  
TEST RESULTS

Material	Weight Change (Mg/Cm <sup>2</sup> ) After 240 Hours at 1750°F
Heat VIII	1.15
Heat IX	0.95
INCO 713C	-4.40
MAR-M-421	-2.20

20 TABLE V  
COMPARATIVE HOT CORROSION  
TEST RESULTS

Material	Depth of Attack (Mils) After 150 Hours at 1650°F with 6 ppm Salt
Heat VIII	4.2
INCO 713C	26.0
MAR-M-421	15.0

- 30 It is not intended that the invention sought to be patented be limited by the foregoing description, but merely by the scope of the appended claims.

#### WHAT WE CLAIM IS:—

- 35 1. A nickel base alloy exhibiting high strength, ductility, sulfidation and oxidation resistance and stability at elevated temperature and consisting of the following in weight percent:

C	—	.30 max.	
Cr	—	11—15	
Co	—	8—12	
Mo	—	1—2.5	40
W	—	3—10	
Ta	—	3.5—10	
Hf	—	0.1—3	
Ti	—	3.5—4.5	
Al	—	3—4	45
Ti+Al	—	7—8	
B	—	0.005—0.025	
Zr	—	.05—.40	
Ni	—	Balance	

2. A nickel base alloy exhibiting high strength, ductility, sulfidation and oxidation resistance and stability at elevated temperature and consisting of the following in weight percent:

C	—	.25 max.	55
Cr	—	11—13.5	
Co	—	8—11	
Mo	—	1—2.5	
W	—	3—5	
Ta	—	3.5—8	60
Hf	—	0.4—3.0	
Ti	—	3.5—4.5	
Al	—	3—4	
Ti+Al	—	7—8	
B	—	0.005—0.025	65
Zr	—	.05—.40	
Ni	—	Balance	

3. A nickel base alloy exhibiting high strength, ductility, sulfidation and oxidation resistance and stability at elevated temperature and consisting of the following in weight percent:

12	1,409,628				12
	C	—	.10—.22	Ta	— 3.65—8
	Cr	—	12.2—13.5	Hf	— 0.75—1.25 25
	Co	—	8.50—9.50	Ti	— 3.9—4.2
	Mo	—	1.85—2.05	Al	— 3.2—3.6
5	W	—	3.65—4.05	Ti+Al	— 7.25—7.70
	Ta	—	3.65—4.05	B	— 0.010—0.020
	Hf	—	0.75—1.25	Zr	— 0.08—0.25 30
	Ti	—	3.90—4.20	Ni	— Balance
	Al	—	3.20—3.60		
10	Ti+Al	—	7.25—7.70	5. A nickel base alloy according to Claim 1 which has been heat treated.	
	B	—	.010—.020	6. A nickel base alloy as claimed in Claims 1 to 5 substantially as hereinbefore described.	35
	Zr	—	0.08—0.25	7. An article formed of the alloy according to any one of the preceding claims.	
	Ni	—	Balance	8. A vacuum cast article consisting of the alloy of any one of the preceding Claims 1 to 6.	40
15	4. A nickel base alloy exhibiting, high strength, ductility, sulfidation and oxidation resistance and stability at elevated temperature and consisting of the following in weight percent:				
	C	—	.10—.22	For the Applicants:—	
20	Cr	—	12.2—13.5	F. J. CLEVELAND & COMPANY,	
	Co	—	8.5—9.5	Chartered Patent Agents,	
	Mo	—	1.85—2.05	Lincoln's Inn Chambers,	
	W	—	3.65—8	40—43 Chancery Lane,	
				London, W.C.2.	

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